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FORCE TO FAIL REACTIONS WITH MONOETHANOLAMINE: APPLICATION TO THE EXPLOSIVE DESTRUCTION SYSTEM

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PREFACE

The work described in this report was authorized under contract nos. DAAD13-03-D-0017 and W911SR-10-D-0004. This work was started in April 2010 and completed in March 2013.

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EXECUTIVE SUMMARY

The Explosive Destruction System (EDS) is a trailer-mounted containment vessel system designed to destroy chemical munitions with or without explosive components. The EDS employs explosive-shaped charges to detonate the munition burster and breach the munition wall exposing the chemical fill material. Once the fill material is exposed, chemical reagents are pumped into the EDS vessel, and the fill material is neutralized. In a recent report, throughput of munitions was cited as an area which could be improved. Increasing the amount of fill material neutralized during each run would be one way to increase throughput. This report summarizes efforts to determine the maximum amount of agent that can be neutralized and still meet the established treatment goals, under typical EDS reaction conditions.

The primary purpose of this effort was to determine the maximum loading of chemical warfare agents (CWA) which could be processed and still meet the treatment goal under typical EDS operating conditions. The intention was not to conduct an investigation into whether the reaction kinetics and product distribution change with increased agent loadings. The primary metric of success was the residual agent concentration remaining in the neutralent. A secondary objective of this effort was to make observations (such as increased viscosity, excessive heat release, and excessive foaming) which will be useful in the optimization process.

GB was successfully neutralized at 30 °C to less than the treatment goal of 1 mg/L when the GB loading was between 30 and 40% and the reaction time was 6 h. During reactions conducted at 45 and 60 °C, GB was successfully neutralized to less than the treatment goal when the GB loading was between 40 and 50%. This is 3–5 times the typical GB loading of 10% used in EDS operations. HD was successfully neutralized at 60 °C to less than the treatment goal of 50 mg/L when the HD loading was between 40 and 50% and the reaction time was 6 h. This is 4–5 times the typical HD loading of 10% used in EDS operations. The treatment goal for HD was not met when the reactions were conducted at 30 and 45 °C using a 20% loading of HD. VX was not reduced below the treatment goal of 1 mg/L under any of the conditions evaluated during this study. In the 1 % VX loading experiments conducted at 60 °C for 6 h, the residual VX was approximately 3 times higher than the treatment goal of 1 mg/L.

The viscosity of the final neutralents, while not determined, appeared to be positively correlated with agent loading, especially for the GB and HD reactions. In reactions conducted at 60 °C, the neutralents became too viscous to stir when the loadings exceeded 60% for GB and 80% for HD. In addition to residual agent concentration, viscosity of the final neutralent obtained at higher agent loadings should be evaluated as part of the decision making process.

A commercially available lanthanum-based catalyst was found to be useful in accelerating the decomposition of VX, but not HD, when the reactions were conducted using a 10% agent loading. The half-life of HD was estimated to be 97 min without the catalyst and 101 min with the catalyst when the reactions were conducted at ambient (~23 °C) temperature. The half-life of VX was estimated to be 246 min without the catalyst and 84 min with the catalyst when the reactions were conducted at 30 °C.

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FORCE TO FAILURE REACTIONS WITH MONOETHANOLAMINE: APPLICATION TO THE EXPLOSIVE DESTRUCTION SYSTEM

1. INTRODUCTION

1.1 Background

The U.S. Army has the mission to provide centralized management and direction to the Department of Defense (DoD) for the safe destruction of all U.S. non-stockpile chemical materiel (NSCM) as defined in Public Law 102-484, 23 October 1992. Destruction of NSCM, including recovered chemical warfare materiel (RCWM), will be in accordance with federal laws, policies, regulations, and directives, as well as applicable state and local laws and regulations. The Army is the DoD focal point for the coordination of all matters relating to NSCM destruction. This is accomplished by developing, constructing, fielding, and supporting the necessary capabilities and materiel used to characterize, contain, transport, store, treat, and dispose of NSCM, both for routine and emergency response scenarios.

RCWM consist of older chemical munitions that have been recovered outside the controlled chemical stockpile. Historically, upon discovery of chemical warfare materiel (CWM), explosive ordnance disposal technicians would identify and assess the condition of the munition and determine whether the ordnance was filled with toxic chemicals and if it was safe for transportation and storage. Chemical munitions that were determined to be safe were overpacked (placed into a container with packing material as appropriate) and stored onsite or transported by the 22nd Chemical Battalion (previously known as U.S. Army Technical Escort Unit) to an appropriate chemical storage facility. Those RCWM items that could not be transported or stored due to unacceptable risks were destroyed onsite using emergency destruction procedures.

The U.S. Army Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) is responsible for the destruction of several categories of chemical warfare materiel in a safe, cost effective, environmentally sound manner and in compliance with the Chemical Weapons Convention.¹ Munitions containing isopropyl methylphosphonofluoridate (GB, sarin, $C_4H_{10}FO_2P$, CAS No. 107-44-8), bis(2-chloroethyl) sulfide (HD, sulfur mustard, $C_4H_8Cl_2S$, CAS No. 505-60-2) and O-ethyl-S-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX, $C_{11}H_{26}NO_2PS$, CAS No. 50782-69-9) are currently in storage and are scheduled to be destroyed using chemical neutralization technologies.²⁻⁵ However, leaking munitions which have been overpacked are not amenable to the primary neutralization technology, and explosive destruction technologies have been recommended to destroy both the overpacked munitions and any reject munitions discovered during operations.^{6,7} To facilitate destruction of these overpacked and reject munitions, PMNSCM has recommended the Explosive Destruction System (EDS) be deployed to treat these items.⁸

1.2 Explosive Destruction System

The EDS is a trailer-mounted containment vessel system designed to destroy chemical munitions with or without explosive components.. The EDS employs explosive-shaped charges to detonate the munition's burster and breach the munition's wall exposing the chemical fill material. Once the fill material is exposed, chemical reagents are pumped into the EDS vessel, and the vessel is then agitated and heated. Once the reaction is complete, typically less than 6 h, the waste material is removed from the EDS vessel and transported to a treatment, storage, and disposal facility (TSDF) for final disposal. The EDS has been successfully used to safely destroy more than 1700 items at eight locations throughout North America and Europe.⁹ This total includes 1200 munitions (mainly 4.2 in. mortars and German Traktor rockets captured during WW II) destroyed at a single location between 2006 and 2010.⁹ The EDS is illustrated in Figure 1.¹⁰

1.3 Study Objectives

The primary purpose of this effort was to determine the maximum loading of chemical warfare agent (CWA) which could be utilized and still meet the treatment goal under typical EDS operating conditions. The intention was not to conduct an investigation into whether the reaction kinetics and product distribution change with increased agent loadings. The primary metric of success was the residual agent concentration remaining in the neutralent. A secondary objective of this effort was to make observations (such as increased viscosity, excessive heat release, and excessive foaming) which will be useful in the down selection process.

1.4 History of Monoethanolamine (MEA) Chemistry

The use of MEA (CAS No. 141-43-5) as a possible decontamination reagent for HD was first reported in 1912.¹¹ During WWI, additional studies were conducted to further explore the use of amines as decontaminants for CWA, particularly HD.¹² In addition to the open literature reports, a significant amount of work was performed at the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC), now ECBC, in the 1970s investigating the reaction of MEA with HD as part of the demilitarization effort.¹³ Until the early 1980s, MEA was approved as a decontaminant for use in USA surety facilities.¹⁴ The investigation of MEA as a neutralization reagent languished during the late 1980s, but was restarted in the mid-1990s. This resurgence of MEA-related research was related to the Russian Federation's decision to use MEA as a reagent for the neutralization of HD, GB and GD.¹⁵ In 1997, a series of reports were published describing the use of MEA for the neutralization of GB, HD and VX.¹⁶⁻¹⁸ The generally accepted major reaction pathways are illustrated in Figure 2.

MEA-based reagents are approved for use in the EDS,¹⁹ and MEA-based reagents have been successfully used in full-scale EDS operations.^{20,21} The MEA-based reagents approved for use in the EDS are: MEA-water mixtures for G and H-class CWA and an MEA-caustic mixture for V-class CWA.¹⁹ The advantages of MEA as a neutralization reagent include good solvent properties for agents, miscibility with water, noncorrosivity to stainless steel under typical EDS operating conditions, and low flammability.¹³ Readers interested in the properties of MEA are referred to a review by Scheiman.²²



Figure 1. Illustrations of the EDS. Upper panel is the overall system and lower panel is 3 munitions being readied for detonation. (Photographs courtesy of U.S. Army¹⁰)

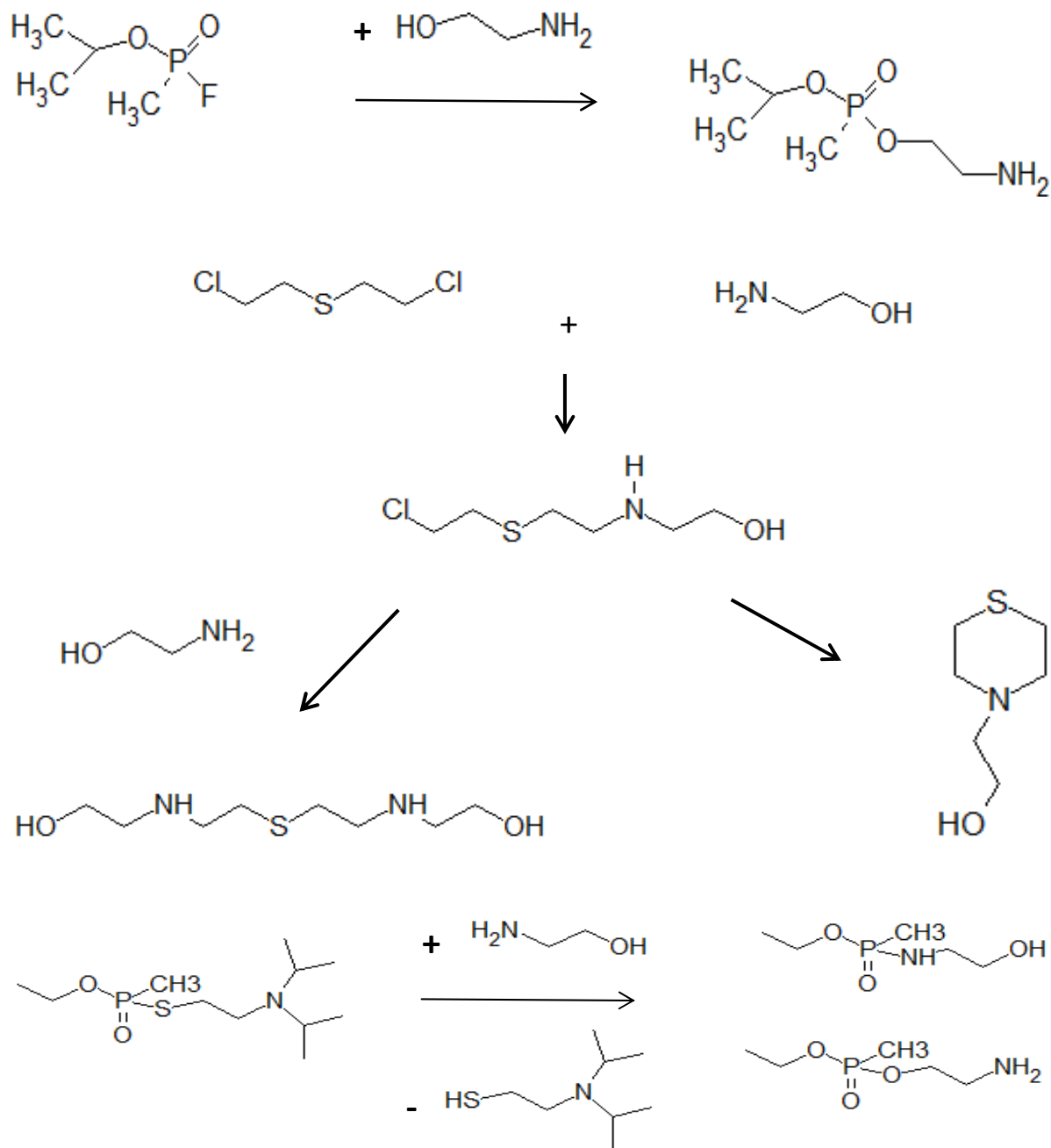


Figure 2. Reaction of CWA with monoethanolamine. Upper panel is GB, middle panel is HD, and lower panel is VX. ¹⁶⁻¹⁸

2. EXPERIMENTAL PROCEDURES

This section describes the in-house experimental procedures and analytical methods utilized during this project.

2.1 Micro-Scale Reaction Studies

The approach of evaluating reagents on a micro-scale was implemented to reduce both the use of hazardous chemicals (thereby minimizing danger to personnel performing the reactions) and the volume of waste generated during the study. In addition to the risk reduction and cost savings realized using this approach, the residual CWA data was not subjected to sampling issues, particularly since the final neutralent contained solids. This is because the extraction was carried out in the same vial the reaction was performed in. It is well documented in the literature that trace organics may adsorb to vial surfaces/solids, requiring the entire sample bottle to be extracted with organic solvent to obtain reliable results.²³⁻²⁵ This micro-scale approach to screening reaction chemistries has been successfully implemented in other studies investigating the chemical neutralization of CWA.²⁶⁻³⁰

While CWA and reagent volumes were varied depending on the experiment, the basic procedure was the same throughout this study. The rusted iron and copper were added to represent the typical *relative* quantities of iron and copper present in the reaction vessel during typical EDS operations. The micro-scale reactions were conducted, in duplicate, using the following protocol:

- Added ~ 320 mg rusted iron and ~1.5 mg of copper and a Teflon coated stir bar (8 × 1.5 mm) to a 40 mL glass vial. The threads of the vial were wrapped with Teflon tape to reduce the possibility of leaks. Each vial was sealed with a cap, with Teflon-lined silicone septa. *NOTE: Weights of rusted iron and copper are based on representative weights obtained on a micro-scoop of rusted iron and a single granule of copper.*
- First added the desired amount of neat CWA, then the desired amount of reagent. The vial was loosely capped and observed for 3–4 min. If no excessive heat and/or off-gassing were observed, proceeded to the next step.
- Tightened cap and transferred vial to a 15 place stirrer/heat-block set to the desired temperature and a stir speed of 300 rpm.
- At predetermined intervals, the sample vials were removed from the stirrer/heat-block and the *entire* vial processed as described in Section 2.5.

In this report, the loading of agent is expressed as a percentage of the reagent, on a volume to volume basis. For example, if 20 μ L of agent was reacted with 1000 μ L of reagent, this would be described as a 2% agent loading. This same loading could also be described as a 1:50 (v:v) agent to reagent ratio.

2.2 Reagents

All chemicals utilized in this study were typically of American Chemical Society (ACS) reagent grade and were used as received from the manufacturers. Monoethanolamine (MEA, $\text{C}_2\text{H}_7\text{NO}$, CAS No. 141-43-5), sodium hydroxide (NaOH , CAS No. 1310-73-2), sodium chloride (NaCl , 99+%, CAS No. 7647-14-5), iron (granular, 99.99+%, 10–40 mesh, CAS No. 7439-89-6), copper (granular, 99.9+%, –10 to 40 mesh, CAS No. 7440-50-8), potassium phosphate, dibasic (K_2HPO_4 , 99+%, CAS No. 7558-11-4), potassium phosphate, monobasic (KH_2PO_4 , 99+%, CAS No. 7778-77-0), potassium carbonate (K_2CO_3 , CAS No. 584-08-7), sodium hydrogen carbonate (NaHCO_3 , CAS No. 144-55-8), glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, CAS No. 64-19-7), ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, CAS No. 631-61-8), 2-propanol ($\text{C}_3\text{H}_8\text{O}$, CAS No. 67-63-0), methanol (CH_4O , CAS No. 67-56-1), 2-(dibutylamino) ethanol (DBAE, $\text{C}_{10}\text{H}_{23}\text{NO}$, 99%, CAS No. 102-81-8), and lanthanum (III) triflate ($\text{C}_3\text{O}_9\text{F}_9\text{S}_3\text{La} \cdot x\text{H}_2\text{O}$, CAS No. 34629-21-5) were obtained from Sigma-Aldrich (Milwaukee, WI, USA). 2,2,4-trimethylpentane (pesticide residue grade, C_8H_{18} , CAS No. 540-84-1), and methylene chloride (pesticide residue grade, CH_2Cl_2 , CAS No. 75-09-2) were purchased from JT Baker (Phillipsburg, NJ). The American Society for Testing and Materials International (ASTM) Type I deionized water (DIW) was obtained from an in-house system (18 megohm·cm; Thermo Scientific Barnstead Nanopure, Dubuque, IA).

2.3 Preparation of Reagents and Buffers

The neutralization reagents utilized in the current study have been approved for use in the EDS to treat specific classes of CWA.¹⁹ The reagent used to neutralize GB was prepared by mixing 45 mL of MEA with 55 mL of deionized water. The reagent used to neutralize HD was prepared by mixing 90 mL of MEA with 10 mL of deionized water. The reagent used to neutralize VX was prepared by mixing 90 mL of MEA with 10 mL of 50 wt/wt% NaOH solution. Once the solutions cooled to room temperature, they were transferred to individual amber glass bottles and stored at room temperature.

The matrix matching solution was prepared by adding 1000 ± 5 mg of DBAE into a 100 mL Class A volumetric flask containing approximately 50 mL of 2-propanol, mixing, then bringing to the mark with 2-propanol. This solution was stored at room temperature in a glass reagent bottle.

The pH 4 extraction buffer was prepared by adding 4.20 ± 0.05 g of glacial acetic acid and 0.85 ± 0.05 g of ammonium acetate into a one-liter class A volumetric flask containing approximately 500 mL of ASTM Type I deionized water. Once the solution cooled to room temperature, the solution was brought to the mark with deionized water. Solids were removed from the buffer by vacuum filtration through a $0.2 \mu\text{m}$ nylon filter (Alltech Associates, Deerfield, IL) and stored at 4°C in an amber glass bottle. This pH 4 buffer has been successfully used to determine residual G-class agents in a previous study.^{31,32}

The pH 7 extraction buffer was prepared by adding 174.0 ± 0.1 g of potassium phosphate, dibasic and 82.4 ± 0.1 g of potassium phosphate, monobasic into a one-liter class A volumetric flask containing approximately 500 mL of ASTM Type I deionized water. Once the solution warmed to room temperature, the solution was brought to the mark with deionized water. Solids were removed from the buffer by vacuum filtration through a $0.2 \mu\text{m}$ nylon filter and stored at 4°C in an amber glass bottle. This pH 7 buffer has been successfully used to determine residual HD in previous studies.^{28,29}

The pH 10 extraction buffer was prepared by adding 13.82 ± 0.05 g of potassium carbonate and 8.40 ± 0.05 g of sodium hydrogen carbonate into a one-liter class A volumetric flask containing approximately 500 mL of ASTM Type I deionized water. Once the solution warmed to room temperature, the solution was brought to the mark with deionized water. Solids were removed from the buffer by vacuum filtration through a $0.2 \mu\text{m}$ nylon filter and stored at 4°C in an amber glass bottle. This pH 10 buffer has been successfully used to determine residual VX in caustic neutralents.^{24,25,30}

2.4 CWA Feedstocks

The neat GB used in this project was obtained through the Chemical Transfer Facility (CTF) and was identified as lot no. GB-S-7119-CTF-N. This lot of GB was stabilized and considered a munition grade of GB. The GB was black in color and was determined to have an average purity of 80.0 wt% using an established gas chromatography/thermal conductivity detector (GC/TCD) protocol.³³

Two lots of neat HD were used in this project and were identified as lot numbers HD-U-3225-CTF-N and HD-U-0050-CTF-N. Lot no. HD-U-3225-CTF-N was obtained through the Chemical Agent Standard Analytical Reference Material (CASARM) program. The CASARM HD was clear and colorless, had a reported purity of 97.1 ± 0.2 mol%, and also contained 1.94 mol% 1,4-dithiane ($\text{C}_4\text{H}_8\text{S}_2$, CAS No. 505-29-3), and 0.21 mol% 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$, CAS No. 107-06-2).³⁴ Lot no. HD-U-0050-CTF-N was obtained through the CTF and was black in color and considered a munitions grade of HD. The munitions grade HD was determined to have an average purity of 94.8 wt% using an established GC/TCD protocol.³³ Experiments were conducted with both CASARM and munitions grade HD to determine if there were significant differences in efficacy between the two grades of HD.

The neat VX used in this project was obtained through the Agent Chemistry Team and was identified as lot number 04-0011-54. This lot of VX was stabilized and considered a munition grade of VX. The VX was clear and colorless, and was determined to have an average purity of 91.1 wt% using an established GC/TCD protocol.³³

2.5 Determination of Residual Agent

2.5.1 Extraction Procedure

The term “matrix-induced chromatographic response enhancement” was coined in the early 1990s to describe a phenomenon whereby the instrument response per unit amount of analyte is significantly different in a sample extract than in a pure solvent.^{35,36} This phenomenon has previously been documented to occur during the determination of residual VX,^{24,25} and the approach of matrix-matching samples and standards was used to normalize the response differences in the current study. A matrix-matching solution consisting of 10,000 mg/L DBAE in 2-propanol was used to matrix-match VX standards and VX sample extracts during this study.

Extractions were typically performed by adding 20.0 mL of extraction solvent to the vial in which the reaction was conducted, capping the vial, then vortexing to mix. Five milliliters of extraction buffer and ~2 grams of KCl were then added to the reaction vial, the vial capped, and the vial vortexed for ~30 seconds.^a The layers were then allowed to separate and the vortexing cycle was repeated two additional times. Once the layers separated, an aliquot of the organic (upper) layer was transferred to a GC vial. In the case of VX extracts, 100 µL of DBAE matrix matching solution was added to each 1000 µL of extract. The vial was closed with a crimp top seal and stored at -20 °C until analyzed. Extraction of GB neutralents was accomplished using the pH 4 buffer/trimethylpentane solvent, extraction of HD neutralents was accomplished using the pH 7 buffer/trimethylpentane solvent, and extraction of VX neutralents was accomplished using the pH 10 buffer/1:1 methylene chloride:trimethylpentane solvent.

Spike recovery data were generated by spiking a mixture (reagent, buffer, KCl and solvent) with agent, and applying the sample preparation and analysis protocols described in Section 2.5. Multiple replicates ($n=7$) were independently prepared and analyzed at a single spike level of 1000 µg/L in the original reagent. In addition to the spiked samples, seven unspiked samples were also prepared and analyzed. In all cases, there was no GB, HD, or VX detected in any of the unspiked samples. The average spike recoveries (\pm SSD) were 72.4 \pm 4.28%, 87.3 \pm 3.21%, and 89.1 \pm 5.82% for GB, HD, and VX, respectively. Overall detection limits were estimated by using the average signal to noise ratio of the quantitation ion, and extrapolating back to the sample concentration that would yield a signal to noise ratio of three. The overall detection limits were estimated to be 52, 61, and 42 µg/L for GB, HD, and VX, respectively. The spike recovery data indicate the analytical method is under control, and suitable for quantitative analysis of GB, HD, and VX in these sample matrices.

2.5.2 Analysis Procedure

The chromatographic column selected for use in this project has been used extensively in other analytical methods and found to be rugged and reliable.^{24,25,28,29} The injection parameters, such as pressure pulse, post-injection dwell time, etc., were selected based on previous experience in our laboratory.^{24,25,28,29}

^a These extraction conditions are based on a 2 mL neutralent volume. If the neutralent volume is changed, extraction solvent, buffer and KCl amounts need to be scaled accordingly.

There were 2 instruments utilized during this study to determine the target analytes. The first was an Agilent Technologies (Santa Clara, CA) Model 6890Plus+ gas chromatograph with an Agilent Model 5975*i* mass selective detector. The second was an Agilent Model 6890N gas chromatograph with an Agilent Model 5973*i* mass selective detector. Helium was used as a carrier gas, at an average linear velocity of 42 cm/s, in pressure pulse mode. All experiments utilized a capillary column with a bonded phase of 5% phenylmethyl polysiloxane (30 m X 0.32 mm) with a 1 μ m film thickness. A 4 mm single gooseneck deactivated liner, with no packing, was utilized. Instrumental parameters are summarized in Table 1.

Primary stocks of each agent were individually prepared from CASARM grade neat agent and were prepared in 2-propanol. Primary stock solutions were prepared on a weight/volume basis, using Class A volumetric glassware. The concentration of each stock solution was ~1000 mg/L, and stock solutions were stored at ~4 °C in a glass vial with a Teflon-faced silicone cap liner. Working standards were prepared by serial dilution of the primary stock with the appropriate solvent. In the case of VX standards, DBAE matching solution was also added to the standards. The linear calibration range was established to be 0.1 to 100 mg/L. Working calibration standards were prepared daily and calibration standards were analyzed with each group of samples. In addition to the calibration standards, reagent blanks were prepared and analyzed concurrently with each batch of samples.

Table 1. Gas Chromatographic Instrumental Parameters

<u>INJECTION PARAMETERS</u>	
Injection Port: 260 °C	Injection Volume: 1.0 μ L, Pulsed Splitless
Injection Pulse: 20 psi for 2 min	Post Injection Dwell: 0.25 min
Sample Washes: 1	Purge Flow: 50 mL/min at 2.50 min
Sample Pumps: 3	Solvent A Washes: 1
Solvent B Washes: 1	Viscosity Delay: 1 s
Solvent A: 2-propanol	Solvent B: Methanol
<u>OVEN PARAMETERS</u>	
Initial Temperature: 50 °C	Initial Time: 3.00 min
Ramp: 12 °C/min to 220 °C and hold for 5 min, then 70 °C/min to 275 °C and hold for 5 min	
Equilibration Delay: 2.0 min	
<u>DETECTOR PARAMETERS</u>	
Solvent Delay: 5.0 min	Resolution: Low
Acquisition Mode: SIM	Dwell Time: 100 ms
MS Source: 230 °C	MS Quads: 150 °C
MS Transfer Line: 280 °C	
Extracted Ions for GB: 81, 93, and 125; used m/z 125 for quantitation.	
Extracted Ions for HD: 109, 111, 158 and 160; used m/z 109 for quantitation.	
Extracted Ions for VX: 114, 139, 224 and 252; used m/z 252 for quantitation.	

3. RESULTS AND DISCUSSION

This section describes the results obtained during this study. An overview of the results is provided in Table 2.

Table 2. Summary of Results. Green cells are conditions where treatment goal was met, yellow cells indicate the residual agent was within $\pm 10\%$ of the treatment goal, and red cells indicate the residual agent was $> 10\%$ of the treatment goal.

Chemical Agent		30 °C			45 °C			60 °C		
		Reaction Time (h)								
Type	Loading (%)	2	4	6	2	4	6	2	4	6
GB	20	Green	Green	Green	Green	Green	Green	Red	Green	Green
	30	Green	Green	Green	Green	Green	Green	Green	Green	Green
	40	Red	Green	Green	Green	Green	Green	Green	Green	Green
	50	Red	Yellow	Green	Green	Green	Green	Red	Green	Green
	60	Red	Red	Green	Green	Green	Green	Green	Red	a
	70	Red	Red	Red	Red	Red	Red	Red	Red	a
HD	20	Red	Red	Red	Red	Yellow	Yellow	Green	Green	Green
	33	Red	Red	Red	Red	Red	Red	Green	Green	Green
	40	Red	Red	Red	Red	Red	Red	Green	Green	Green
VX	1	b	b	b	b	b	Red	b	b	Red
	2	b	b	b	b	b	Red	b	b	Red
	3	b	b	b	b	b	Red	b	b	Red
	4	b	b	b	b	b	Red	b	b	Red
	5	b	b	b	b	b	Red	b	b	Red

a. Neutralent became too viscous to stir.

b. No data collected at these conditions.

3.1 Neutralization of GB

An initial series of range finding reactions were conducted at 60 °C, with GB loadings ranging from 20–100 %. In all cases, reactions were conducted in duplicate, with a reaction time of 6 h. There were no anomalies noted during these reactions and all analytical quality control (QC) samples were within acceptable limits. There was no GB detected in any of the laboratory solvent blanks ($n=6$) or MEA reagent blanks ($n=3$). The results of the range-finding experiment are summarized in Table 3 and Figure 3. The treatment goal of 1 mg/L was exceeded as the loading increased from 50–60%.

Table 3. Reaction Conditions and Residual GB During the Range Finding Experiment. In all cases the reactions were conducted at 60 °C for 6 h.

Reagent Added (μL)	GB Added (μL)	GB Loading (%)	Residual GB in Neutralent (mg/L)	
			Replicate One	Replicate Two
1000	200	20	0.30	0.40
1000	300	30	0.32	0.33
1000	400	40	0.45	0.37
1000	500	50	0.88	0.92
1000	600	60	1.95	1.80
1000	700	70	6.83	6.69
1000	800	80	18.6	19.4
1000	900	90	158	202
1000	1000	100	1010	675

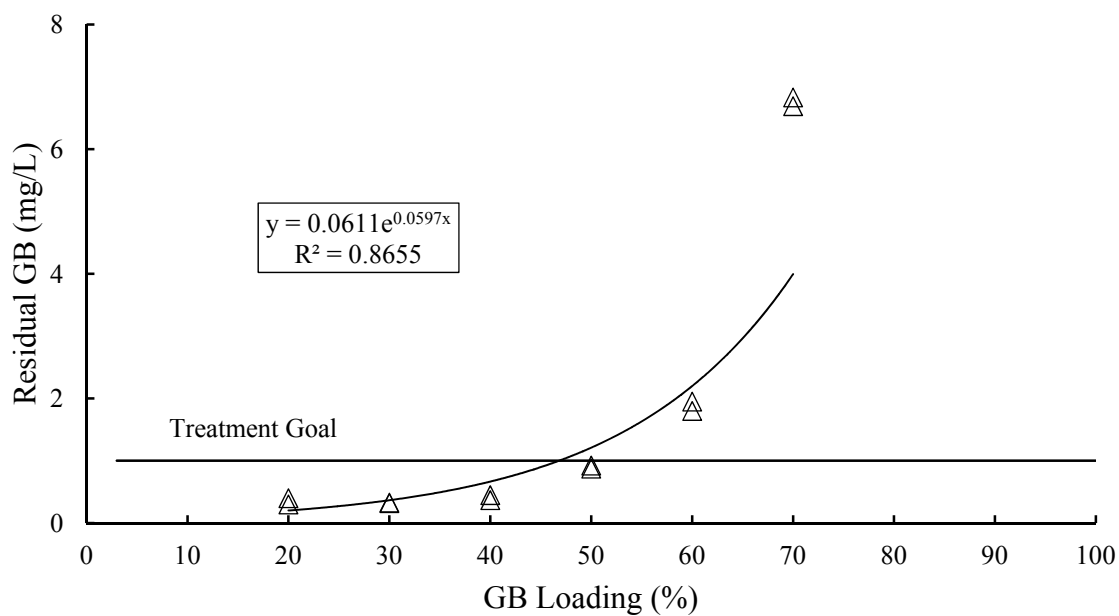
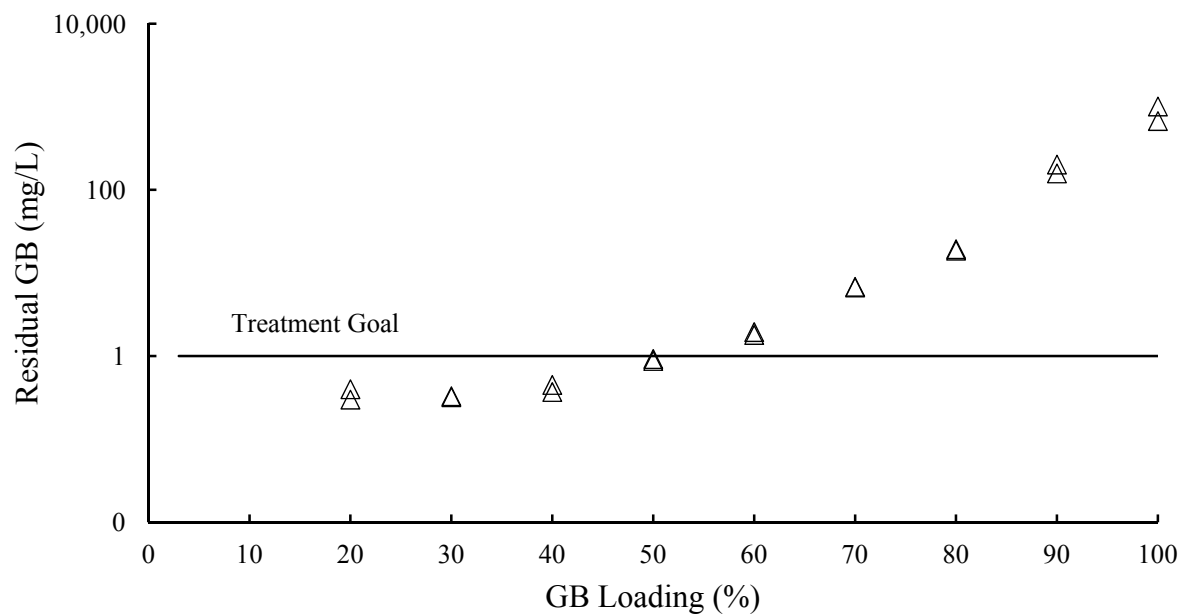


Figure 3. Residual GB as a function of agent loading during the range finding experiment. Upper panel is full scale, with the Y-axis on a log scale. Bottom panel is zoomed in to a smaller range. Reactions conducted for 6 h at 60 °C.

Based on results from the range finding experiment, a second series of reactions were conducted to investigate reagent efficacy as a function of time and temperature, with GB loadings ranging from 20–70 %. Reaction temperatures of 30, 45, and 60 °C and reaction times of 2, 4, 6, and 24 h were evaluated during these experiments. In all cases, reactions were conducted in duplicate. There was no foaming or excessive heat generation observed during these reactions. *However, it was observed that the 24 h samples from the 60 °C reactions (60 and 70% loadings only) stopped stirring sometime during the reaction.* All analytical QC samples were within acceptable limits. There was no GB detected in any of the laboratory solvent blanks ($n=9$) or MEA reagent blanks ($n=3$). The results are summarized in Tables 4–6 and Figure 4.

In a reported study examining the reaction of GB with MEA, the final neutralent was noted to be “*very viscous, probably as a result of hydrogen bonding between MEA and HF*”³⁷. The reported study utilized a 90:10 (v:v) MEA:water mixture as the reagent and the reaction was conducted at ambient temperature (~23 °C). The GB loadings examined in the reported study were 10 and 100%, with the neutralent generated from the 100% loading being the most viscous.

Similar issues with viscosity were observed in the current study, with reactions conducted at 60 °C and loadings of 60 and 70% becoming so viscous the stir bars were unable to mix the neutralent. This decrease in mixing might account for the increased GB concentrations measured for these reactions. It was observed that the 2 h time points, in general, tended to be more scattered and elevated. This might be due to a reaction time that was too short. Eliminating the 2 h time points and the samples that stopped stirring, the pooled results are illustrated in Figure 5. There is an increase in variability when the GB loading is at or above 40%, which might be related to an increase in viscosity of the neutralent.

Overall, GB was successfully neutralized at a loading between 30 and 40%, when the reaction was conducted at 30 °C. This is 3–4 times the standard loading of 10% (1:10 agent to reagent ratio). If the reaction temperature is increased to 45 °C, GB can be successfully neutralized at a loading between 40 and 50%, which is 4–5 times the standard loading of 10%. Increasing the reaction temperature to 60 °C did not increase the loading capacity and the higher temperature resulted in significantly more viscous neutralents.

Table 4. Reaction Conditions and Residual GB During the 30 °C Experiment. In all cases the reactions were conducted in duplicate.

Reagent Added (μL)	GB Added (μL)	GB Loading (%)	Residual GB in Neutralent (mg/L)			
			2 h	4 h	6 h	24 h
1000	200	20	0.16	0.18	0.19	NA ^a
			0.15	0.14	0.17	NA ^a
1000	300	30	0.49	0.29	0.19	NA ^a
			0.54	0.31	0.32	NA ^a
1000	400	40	2.04	0.54	0.41	NA ^a
			1.56	0.95	0.54	NA ^a
1000	500	50	1.95	1.11	0.89	0.96
			1.57	0.97	0.81	0.93
1000	600	60	1.48	1.25	0.81	0.79
			1.35	1.08	0.85	0.85
1000	700	70	2.61	1.84	1.74	1.61
			2.39	1.97	1.64	1.57
a. NA is not applicable. No runs were conducted for 24 h.						

Table 5. Reaction Conditions and Residual GB During the 45 °C Experiment. In all cases the reactions were conducted in duplicate.

Reagent Added (μL)	GB Added (μL)	GB Loading (%)	Residual GB in Neutralent (mg/L)			
			2 h	4 h	6 h	24 h
1000	200	20	0.09	0.09	0.15	NA ^a
			0.11	0.09	0.10	NA ^a
1000	300	30	0.15	0.17	0.14	NA ^a
			0.15	0.15	0.15	NA ^a
1000	400	40	0.33	0.22	0.19	NA ^a
			0.27	0.18	0.20	NA ^a
1000	500	50	1.06	0.61	0.62	0.59
			0.63	0.49	0.68	0.67
1000	600	60	0.99	0.90	0.79	0.69
			0.87	0.89	0.64	0.64
1000	700	70	2.19	1.90	1.71	1.73
			1.91	2.04	1.96	2.79
a. NA is not applicable. No runs were conducted for 24 h.						

Table 6. Reaction Conditions and Residual GB During the 60 °C Experiment In all cases the reactions were conducted in duplicate.

Reagent Added (μL)	GB Added (μL)	GB Loading (%)	Residual GB in Neutralent (mg/L)			
			2 h	4 h	6 h	24 h
1000	200	20	1.59 ^a	0.43	0.30	NA ^b
			1.93 ^a	0.27	0.40	NA ^b
1000	300	30	0.40	0.27	0.32	NA ^b
			0.37	0.40	0.33	NA ^b
1000	400	40	0.44	0.37	0.45	NA ^b
			0.53	0.34	0.37	NA ^b
1000	500	50	2.12	0.88	0.92	0.59
			1.23	0.79	0.63	0.36
1000	600	60	0.495	1.46	1.87	1.24 ^c
			0.842	1.57	1.15	3.02 ^c
1000	700	70	2.61	4.24	2.78	5.82 ^c
			2.86	2.88	3.15	4.80 ^c
a. The reason for these elevated GB concentrations is not known.						
b. NA is not applicable. No runs were conducted for 24 h.						
c. Samples became too viscous; stir bar was not able to mix neutralent.						

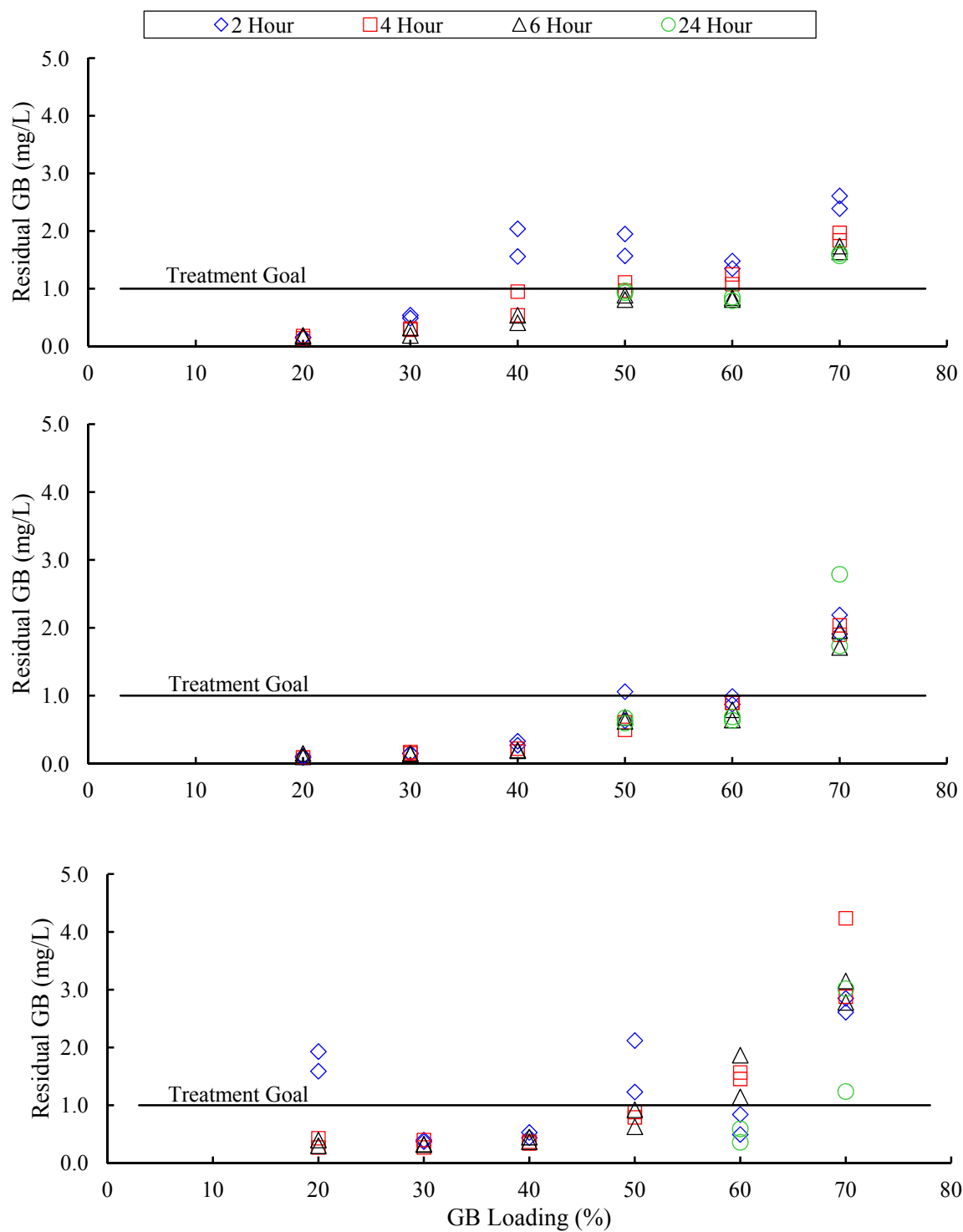


Figure 4. Residual GB as a function of agent loading and reaction time. Upper panel is reaction at 30 °C, middle panel is reaction at 45 °C, and bottom panel is reaction at 60 °C.

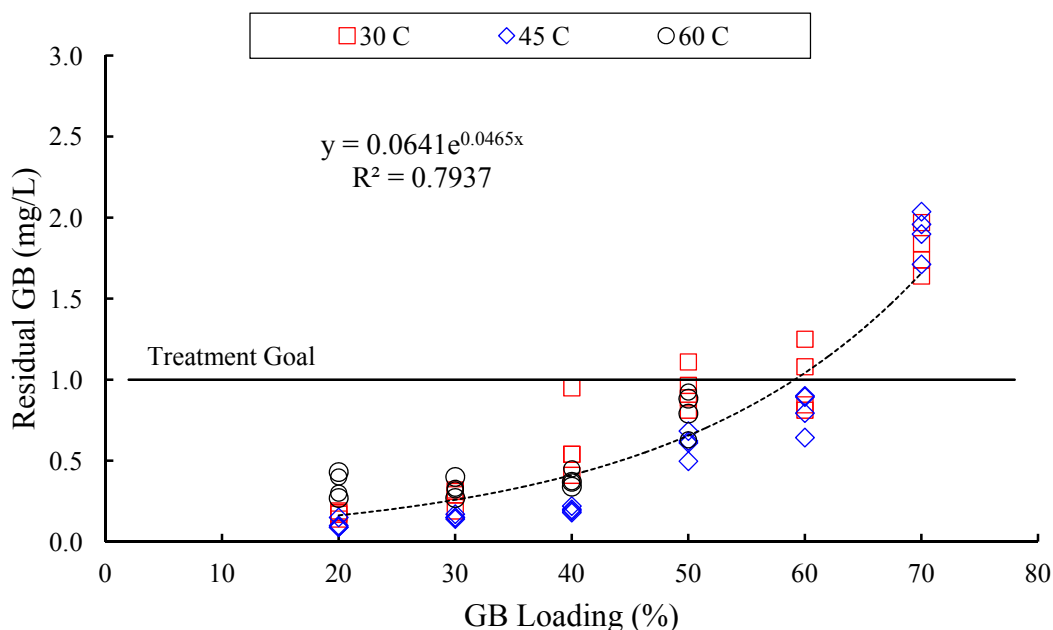


Figure 5. Pooled residual GB as a function of agent loading. The 4 and 6 h reaction time data from all runs was pooled. The 60 and 70% loading data from the 60 °C treatment were not included in the pooled data.

3.2 Neutralization of HD

An initial series of range finding reactions were conducted at 60 °C, with HD loadings ranging from 2–100 % when using CASARM grade HD and 20–100% when using munition grade HD. In all cases, reactions were conducted in duplicate, with reaction times of 6 and 24 h during the CASARM runs and 6 h during the munition grade runs. There were no anomalies noted during the reactions when HD loadings were below 50%. However, when the HD loading was $\geq 50\%$, noticeable amounts of heat were generated and white fumes were observed to form when the reagent was added to the HD. In addition, when the HD loading was 80% and higher, the stir bars were unable to stir the neutralent due to the increased viscosity. All analytical QC samples were within acceptable limits. There was no HD detected in any of the laboratory solvent blanks ($n=12$) or MEA reagent blanks ($n=4$). The results of the range-finding experiments are summarized in Tables 7 and 8 and Figures 6 through 8. The treatment goal of 50 mg/L was exceeded as the loading increased from 50–60%. As illustrated in Figure 8, there does not appear to be any significant difference in efficacy when munition grade HD is neutralized.

Table 7. Reaction Conditions and Residual HD During the CASARM Grade Range Finding Experiment In all cases the reactions were conducted at 60 °C and in duplicate.

Reagent Added (μL)	HD Added (μL)	HD Loading (%)	Residual HD in Neutralent (mg/L)	
			6 h	24 h
2000	40	2	0.02	Trace ^a
			0.04	Trace ^a
2000	100	5	0.03	0.02
			0.10	0.02
2000	200	10	0.08	0.04
			0.16	0.05
1000	100	10	0.12	0.03
			0.13	0.03
1000	125	12.5	0.23	0.05
			0.31	0.06
1000	150	15	0.26	0.07
			0.21	0.08
1000	200	20	0.36	0.09
			0.33	0.10
250	50	20	0.60	0.09
			0.52	0.11
200	50	25	0.99	0.19
			0.98	0.10
150	50	33.3	1.40	0.66
			2.66	0.81
100	50	50	78.1	0.61
			14.1	0.84
50	50	100	175,000 ^b	75,300 ^b
			167,000 ^b	95,300 ^b
a. Trace detection.				
b. Samples became too viscous; stir bar was not able to mix neutralent.				

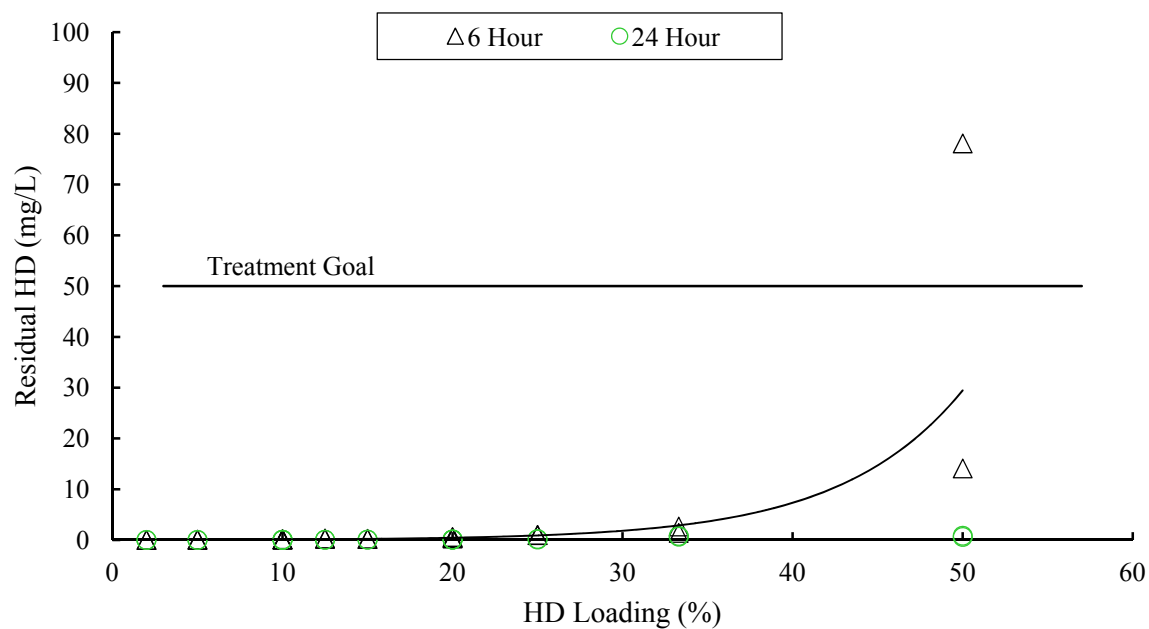
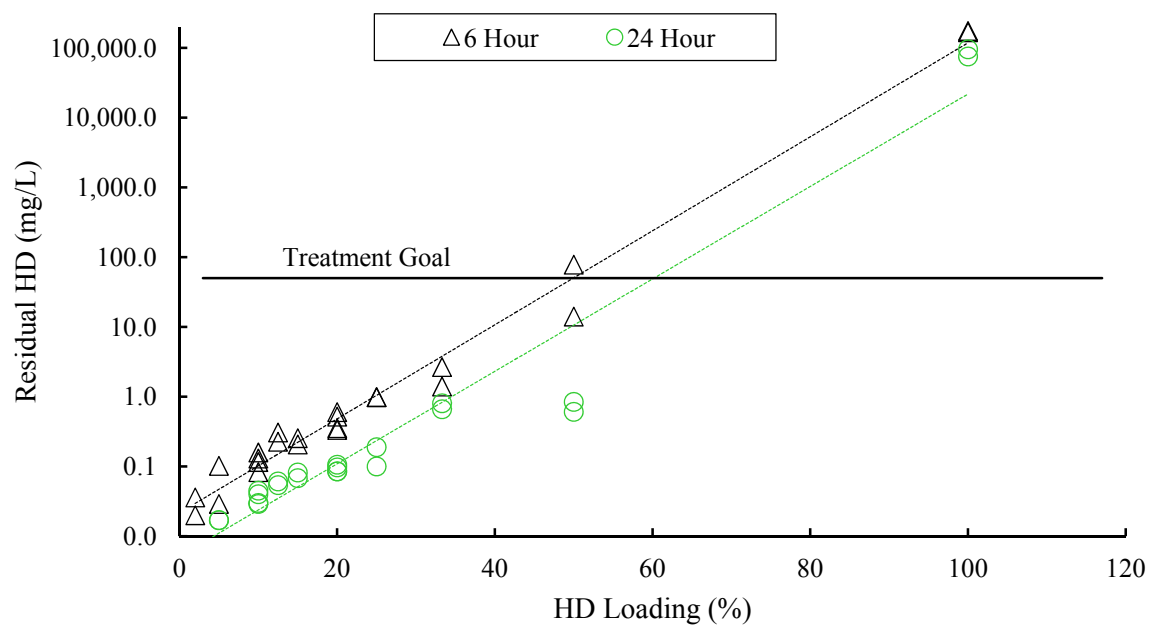


Figure 6. Residual HD as a function of agent loading in the CASARM HD range finding experiment. All reactions conducted at 60 °C. Note the y-axis in the upper panel is a log scale.

Table 8. Reaction Conditions and Residual HD During the Munitions Grade Range Finding Experiment In all cases the reactions were conducted at 60 °C for 6 h and were conducted in duplicate.

Reagent Added (μL)	HD Added (μL)	HD Loading (%)	Residual HD in Neutralent (mg/L)	
			Replicate One	Replicate Two
1000	200	20	2.70	4.12
1000	330	33	3.10	4.40
1000	400	40	8.91	6.46
1000	500	50	50.7	45.2
1000	600	60	106	111
1000	700	70	357	741
1000	800	80	12,100 ^a	15,600 ^a
1000	900	90	13,100 ^a	24,800 ^a
1000	1000	100	71,100 ^a	55,700 ^a
a. Samples became too viscous; stir bar was not able to mix neutralent.				

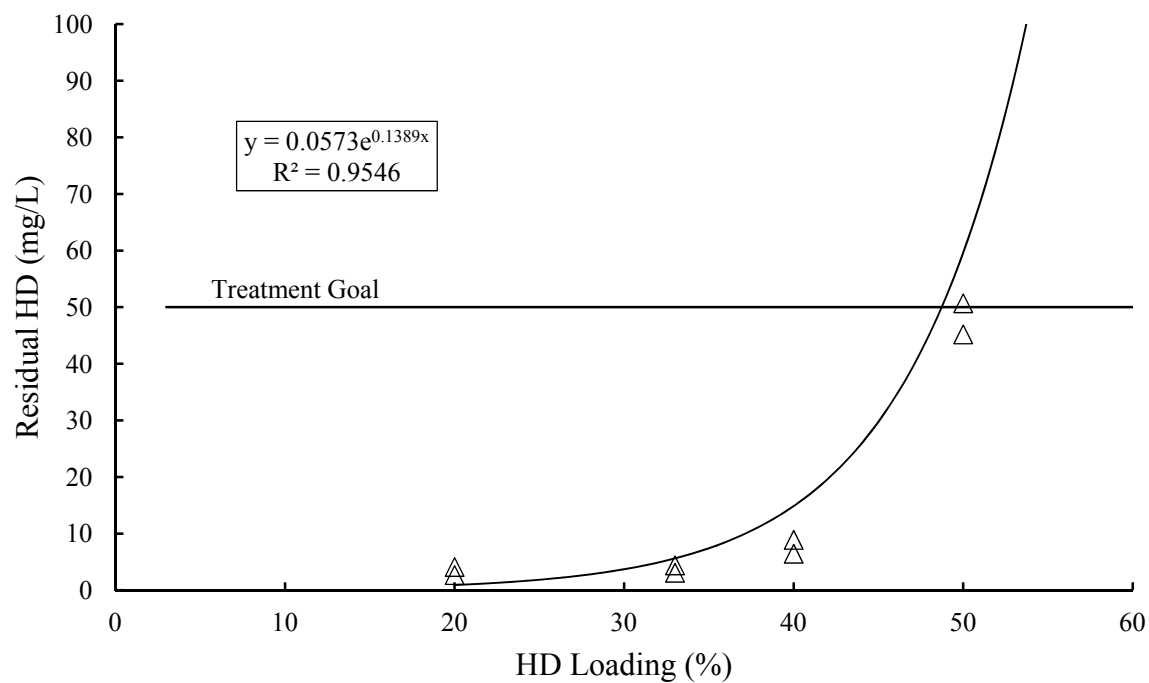
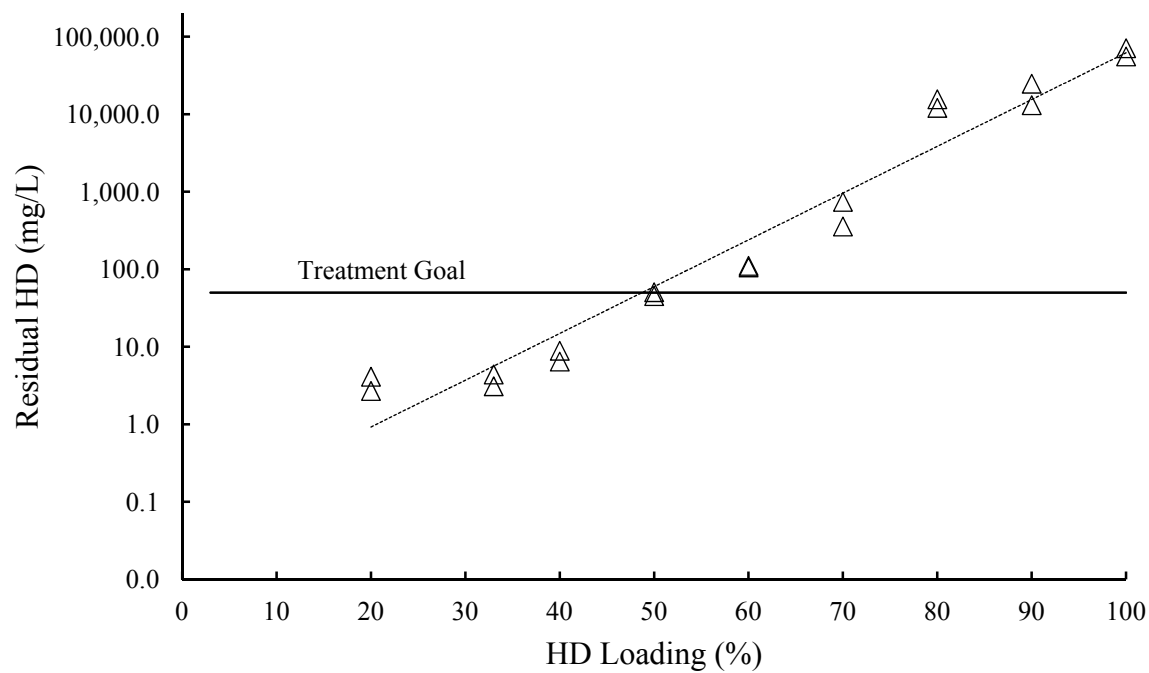


Figure 7. Residual HD as a function of agent loading in the munitions HD range finding experiment. All reactions conducted at 60 °C. Note the y-axis in the upper panel is a log scale.

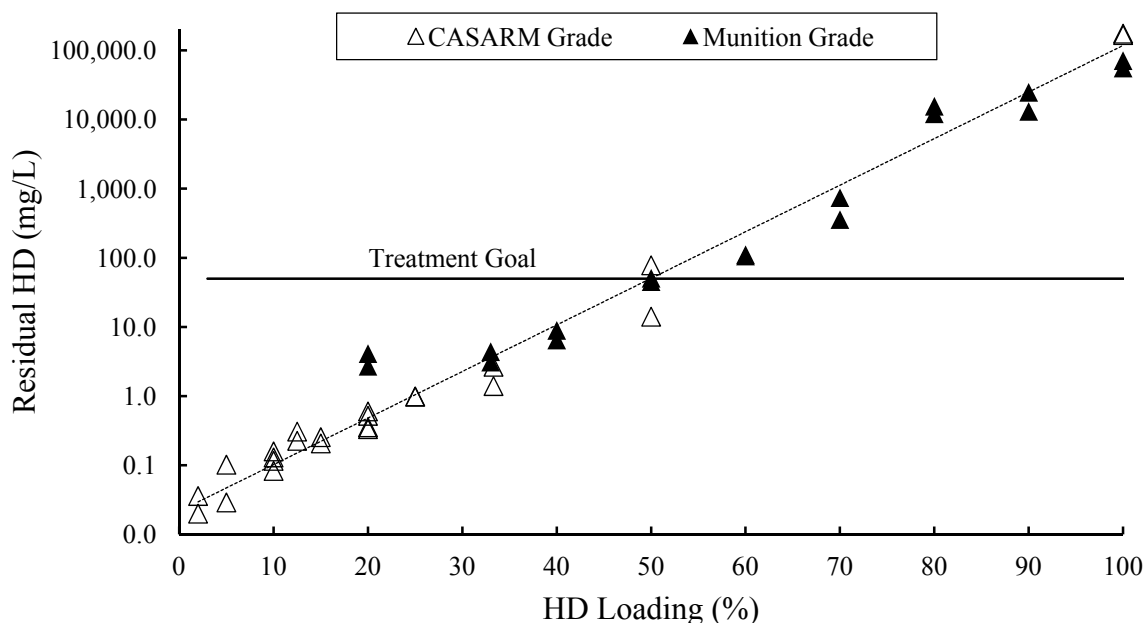


Figure 8. Comparison of CASARM and munition grade HD. In all cases, reactions were conducted at 60 °C for 6 h. Note the Y-axis is a log scale.

Based on results from the range finding experiment, a second series of reactions were conducted to investigate reagent efficacy as a function of time and temperature, with munitions grade HD loadings ranging from 20–40 %. Reaction temperatures of 30, 45, and 60 °C and reaction times of 2, 4, 6, and 24 h were evaluated during these experiments. In all cases, reactions were conducted in duplicate. There were no anomalies observed during these reactions and all analytical QC samples were within acceptable limits. There was no HD detected in any of the laboratory solvent blanks ($n=6$) or MEA reagent blanks ($n=2$). The results are summarized in Table 9 and Figure 9. Overall, it appears HD can be successfully neutralized at a loading of 40% when the reaction is conducted at 60 °C. This is 4 times the standard loading of 10% (1:10 agent to reagent ratio).

In a reported study examining the reaction of HD with MEA, viscosity of the final neutralent was found to vary, depending on the loading of HD.³⁸ The reported study utilized a 90:10 (v:v) MEA:water mixture as the reagent and the reaction was conducted at temperatures ranging from 0 to 95 °C. In reactions conducted at 60 °C, the viscosity (all viscosities at 25 °C) of the final neutralent ranged from 34.8 ± 0.04 cs at a 10% HD loading, to 86.3 ± 0.2 cs at a 30% HD loading. Using a linear ($r^2=0.9897$) regression model, the viscosity at a 40% HD loading would be 110 cs. For comparison, the reported viscosity for the MEA reagent was 19.5 cs. The same study reported viscosities of 3.12 cs for CASARM HD and 3.54 cs for munition grade HD.³⁸

Table 9. Reaction Conditions and Residual HD During the Time-Temperature Experiment. In all cases the reactions were conducted in duplicate using the munition grade HD.

Reagent Added (μL)	HD Added (μL)	HD Loading (%)	Residual HD in Neutralent (mg/L)		
			2 h	4 h	6 h
Reaction at 30 °C					
1000	200	20	97,400	36,200	9,380
			100,000	29,400	5,150
1000	330	33	253,000	190,000	128,000
			264,000	206,000	131,000
1000	400	40	310,000	253,000	194,000
			298,000	237,000	206,000
Reaction at 45 °C					
1000	200	20	257	60.4	47.0
			207	45.4	55.3
1000	330	33	876	64.8	71.5
			468	66.3	90.5
1000	400	40	1540	86.7	90.0
			1380	81.7	70.2
Reaction at 60 °C					
1000	200	20	21.9	6.87	2.70
			19.8	7.25	4.13
1000	330	33	15.8	9.70	3.10
			13.4	12.9	4.40
1000	400	40	27.9	16.7	8.91
			33.4	14.9	6.46

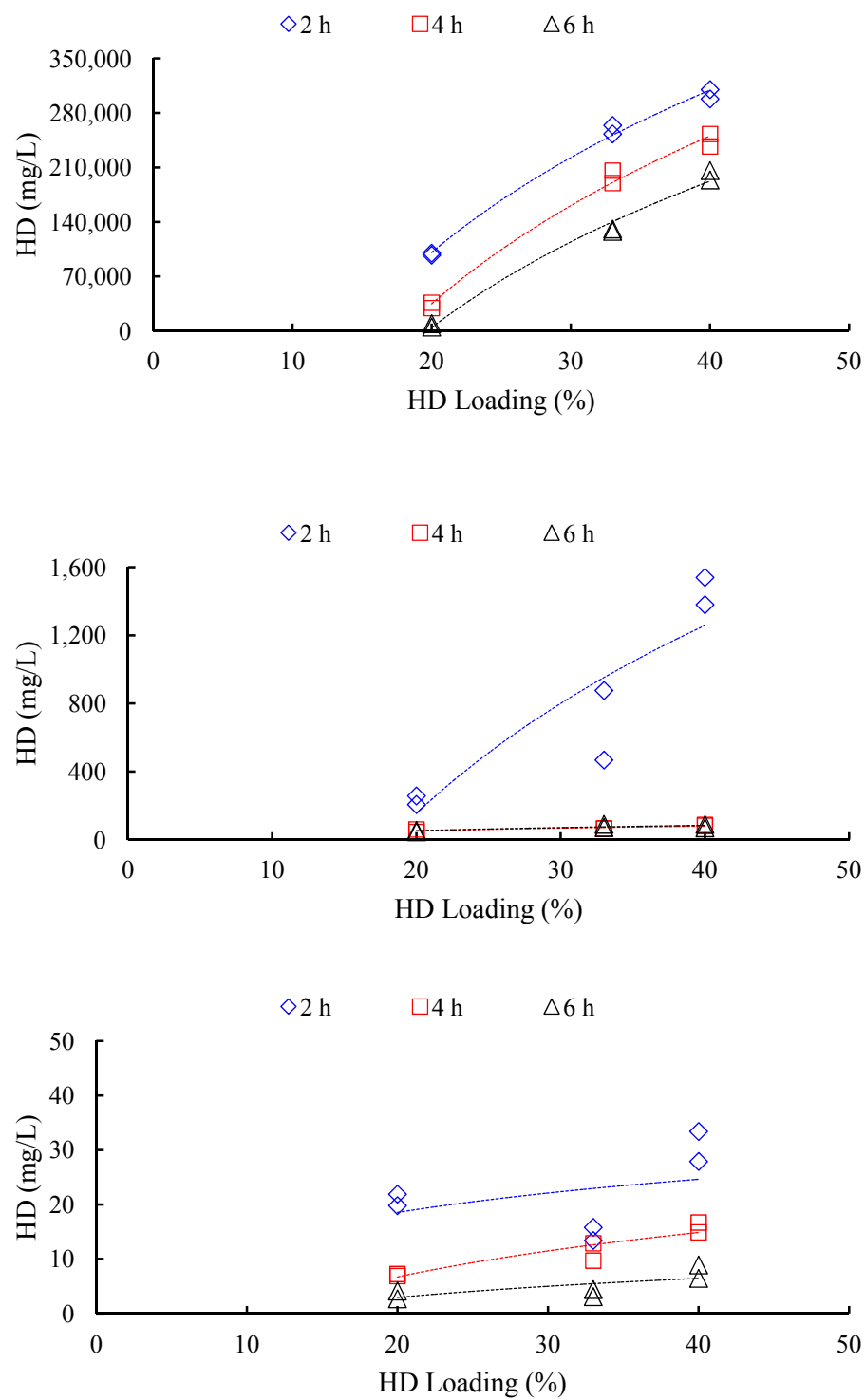


Figure 9. Residual HD as a function of time, temperature and loading. Upper panel is 30 °C, middle panel is 45 °C, and bottom panel is 60 °C.

3.3 Neutralization of VX

An initial series of range finding reactions were conducted at 60 °C, with VX loadings ranging from 10–50 %. In all cases, reactions were conducted in duplicate, with a reaction time of 6 h. There were no anomalies observed during these reactions and all analytical QC samples were within acceptable limits. There was no VX detected in any of the laboratory solvent blanks ($n=4$) or MEA reagent blanks ($n=1$). The results of the range-finding experiments are summarized in Table 10. The treatment goal of 1 mg/L residual VX was not achieved under any of the conditions evaluated in the range finding experiment. The residual VX was approximately 17 times the treatment goal when the VX loading was 10%.

Table 10. Reaction Conditions and Residual VX During the Range Finding Experiment. In all cases the reactions were conducted at 60 °C for 6 h.

Reagent Added (μL)	VX Added (μL)	VX Loading (%)	Residual VX in Neutralent (mg/L)	
			Replicate One	Replicate Two
1000	100	10	17.1	17.6
1000	200	20	42.5	56.9
1000	300	30	165	195
1000	400	40	255	313
1000	500	50	464	669

Based on results from the range finding experiment, a second series of reactions were conducted to investigate reagent efficacy as a function of temperature, with VX loadings ranging from 1–5 %. Reaction temperatures of 45 and 60 °C and a single reaction time of 6 h were evaluated during these experiments. In all cases, reactions were conducted in duplicate. There were no anomalies observed during these reactions and all analytical QC samples were within acceptable limits. There was no VX detected in any of the laboratory solvent blanks ($n=3$) or MEA reagent blanks ($n=1$). The results are summarized in Table 11 and Figure 10. Under the conditions evaluated in this experiment, the treatment goal of 1 mg/L was not achieved. In the lowest VX loading (1%) conducted at 60 °C, the residual VX was approximately 3 times higher than the treatment goal.

Table 11. Reaction Conditions and Residual VX During the Loading Temperature Experiment.
In all cases the reactions were conducted at 60 °C for 6 h.

Reagent Added (μL)	VX Added (μL)	VX Loading (%)	Residual VX in Neutralent (mg/L)	
			45 ° C	60 ° C
1000	10	1	15.7	2.96
			9.33	2.85
1000	20	2	27.3	4.80
			27.0	5.12
1000	30	3	27.3	11.8
			30.6	12.0
1000	40	4	41.7	9.51
			36.6	10.6
1000	50	5	52.7	12.3
			51.9	13.2

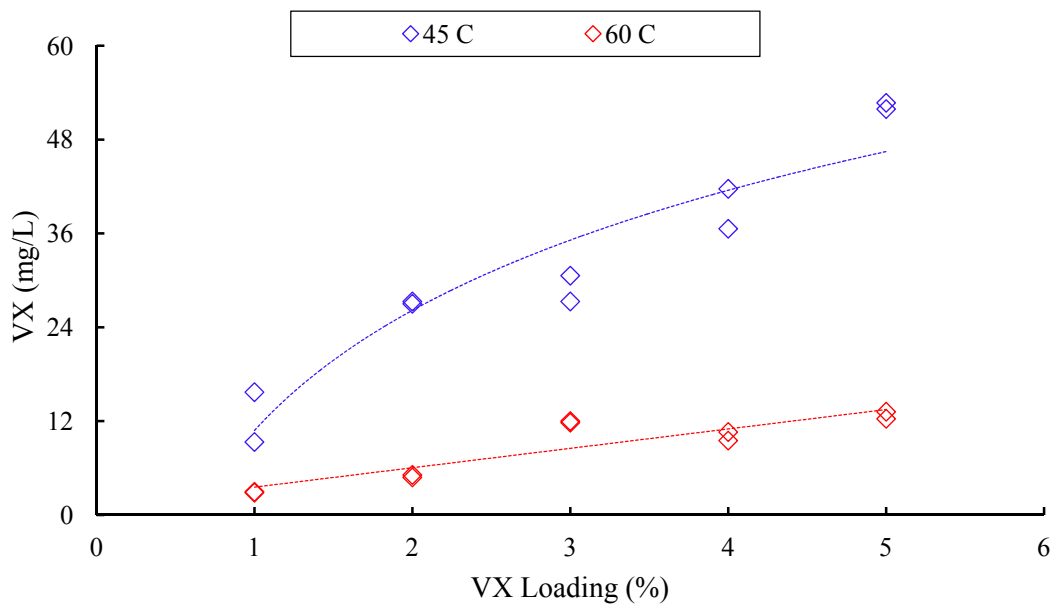


Figure 10. Residual VX as a function of loading and temperature. In all cases the reaction time was 6 h.

In the current study, the 1 mg/L VX treatment goal was not met under any of the conditions evaluated. This is in contrast to a reported study, where the treatment goal was achieved.²⁰ One difference between the current study and the reported study is the reported reaction times. In the current study a reported reaction time of 6 h means 6 h has elapsed from when the sample vial was placed into the heating block and when the extraction was started. In the current study, samples were placed into the heating block within a couple of minutes of mixing the reagent and VX, so there is little lag time in the entire neutralent reaching 60 °C. During EDS operations, once the sample is collected from the EDS vessel, the sample bottle must be transported to an analytical laboratory and downloaded from the sample bottle before the neutralent can be extracted. These additional steps can result in additional time (1–3 h) elapsing from when the 6 h sample is collected and when it is extracted. Alkaline neutralents are still quite reactive towards VX. In reported studies examining the reaction of VX with sodium hydroxide neutralent, it was demonstrated VX was quickly degraded by the alkaline neutralent, even at room temperature.^{24,25} The half-life of VX in these alkaline neutralents was estimated to be 15 minutes, as evidenced by spiking the neutralent and tracking the degradation over short time frames. In the case of the 5% VX loading in this study, the residual VX would be below the treatment goal of 1 mg/L after a 1 h delay between sampling and extraction. It is difficult to make direct comparisons of the results obtained during this study to reported values, unless actual times can be obtained.

3.4 Efficacy of a Catalyst

In reported studies, the use of a commercially available lanthanum-based catalyst (lanthanum(III) triflate) was found to be useful in accelerating the decomposition of phosphorus-based chemical warfare agents.³⁹⁻⁴¹ In an attempt to achieve the treatment goal for HD at a lower temperature, the use of this catalyst was explored in this study. In this experiment, reactions were conducted on a larger scale (2 mL CASARM HD and 20 mL MEA reagent) at a 10% HD loading. Time point samples (500 µL) were removed and extracted, rather than extracting the entire vial as described in Section 2.5.1. Reactions were conducted at ambient temperature (~23 °C) with 0.25 mM catalyst and without catalyst in the MEA reagent.^b A reaction at 60 °C without catalyst was also conducted. There were no anomalies observed during these reactions and all analytical QC samples were within acceptable limits. There was no HD detected in any of the laboratory solvent blanks ($n=3$) or MEA reagent blanks ($n=1$ each type). The results are summarized in Figure 11. Under these experimental conditions, the lanthanum-based reagent did not accelerate the degradation of HD. Using a first-order model, the solution half-life of HD was estimated to be 97 min without the catalyst and 101 min with the catalyst. In comparison, the HD solution half-life at 60 °C was estimated to be < 6 min. In both reactions conducted at ambient temperature, the 50 mg/L treatment goal was not reached, even after 6 h of reaction. In contrast, the treatment goal was reached in approximately 1 h when the reaction was conducted at 60 °C without catalyst.

b. Reaction conditions selected after discussion with Dr. H. DuPont Durst of ECBC who is actively working with this catalyst. He indicated the catalyst would work with MEA, though no experiments had been conducted with HD.

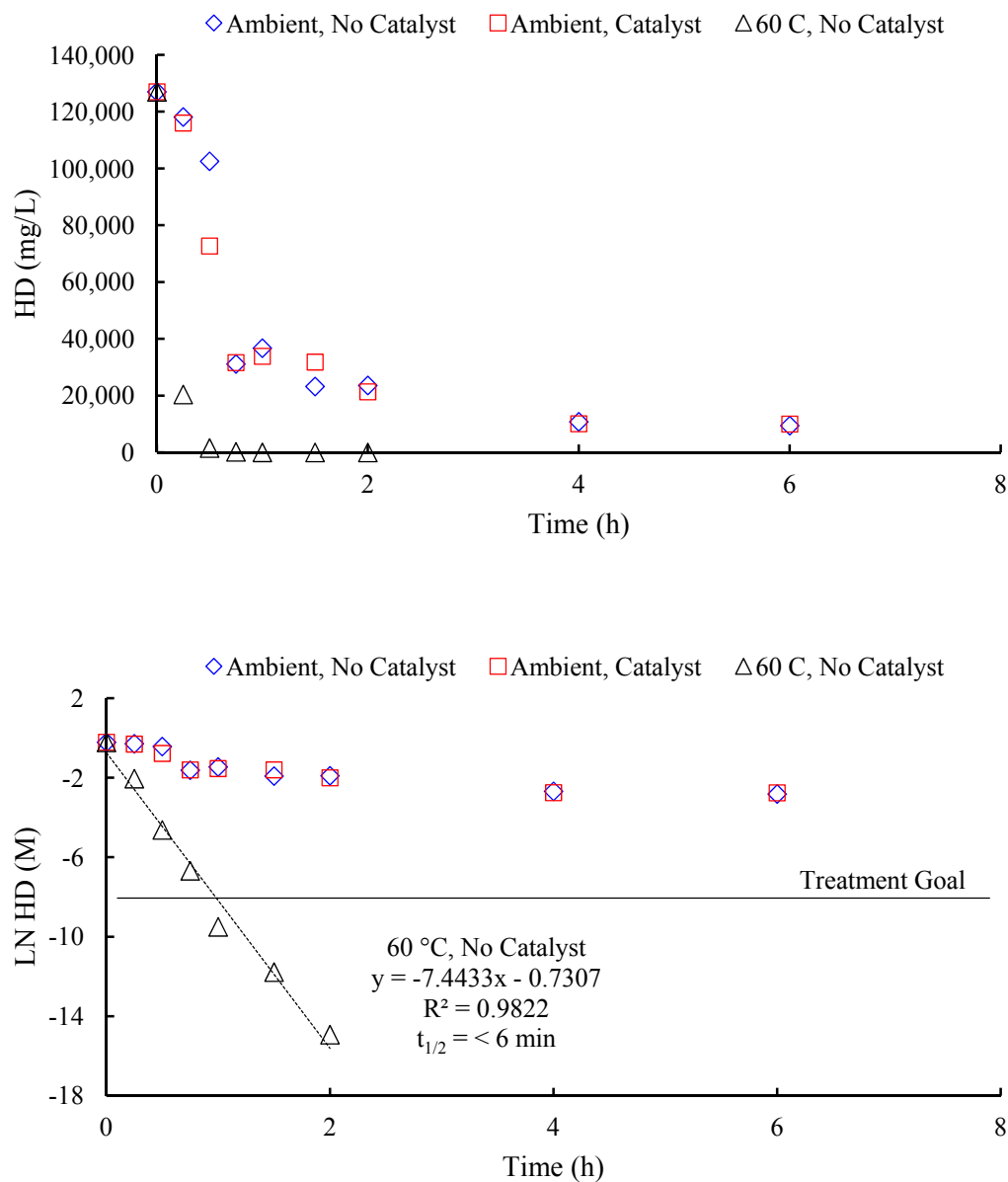


Figure 11. Residual HD as a function of time and catalyst. The HD loading was 10% and CASARM HD was used. Upper panel is the concentration profile and lower panel is the first-order plot.

In an attempt to achieve the treatment goal for VX at a lower temperature, the use of this catalyst was explored in this study. In this experiment, reactions were conducted at 30 °C for 2, 4 and 6h. In all cases, the VX loading was 10%. Reactions were conducted with 0.25 mM catalyst and without catalyst in the MEA reagent.^c There were no anomalies observed during

c. Reaction conditions selected after discussion with Dr. H. DuPont Durst of ECBC who is actively working with this catalyst. He indicated the catalyst had been demonstrated to work with VX in MEA. In reactions conducted at room temperature (~23 °C), the maximum VX loading with non-detect VX concentrations was 17 %. Detection was achieved using NMR, so detection limits are higher than the treatment goal required for EDS operations.

these reactions and all analytical QC samples were within acceptable limits. There was no VX detected in any of the laboratory solvent blanks ($n=2$) or MEA reagent blanks ($n=1$ each type). The results are summarized in Table 12 and Figure 12. Under these experimental conditions, the lanthanum-based reagent did significantly accelerate the degradation of VX. Using a first-order model, the solution half-life of VX was estimated to be 246 min without the catalyst and 84 min with the catalyst. In both cases, the 1 mg/L treatment goal was not reached, even after 6 h of reaction. The average residual VX in the catalyst treatment was 9.7 mg/L, compared to 66.0 when the catalyst was not present. In the 10% VX loading range finding experiment (Table 10), the average residual VX was 17.4 mg/L when the reaction was conducted at 60 °C for 6 h.

Table 12. Reaction Conditions and Residual VX During the Catalyst Experiment. In all cases the reactions were conducted at 30 °C using a 10% VX loading.

Reagent Added (μL)	VX Added (μL)	Time (h)	Residual VX in Neutralent (mg/L)	
			No Catalyst Added	Catalyst Added
1000	100	2	118	77.0
			144	72.9
1000	100	4	94.7	35.6
			103	34.3
1000	100	6	65.7	9.30
			66.3	10.1

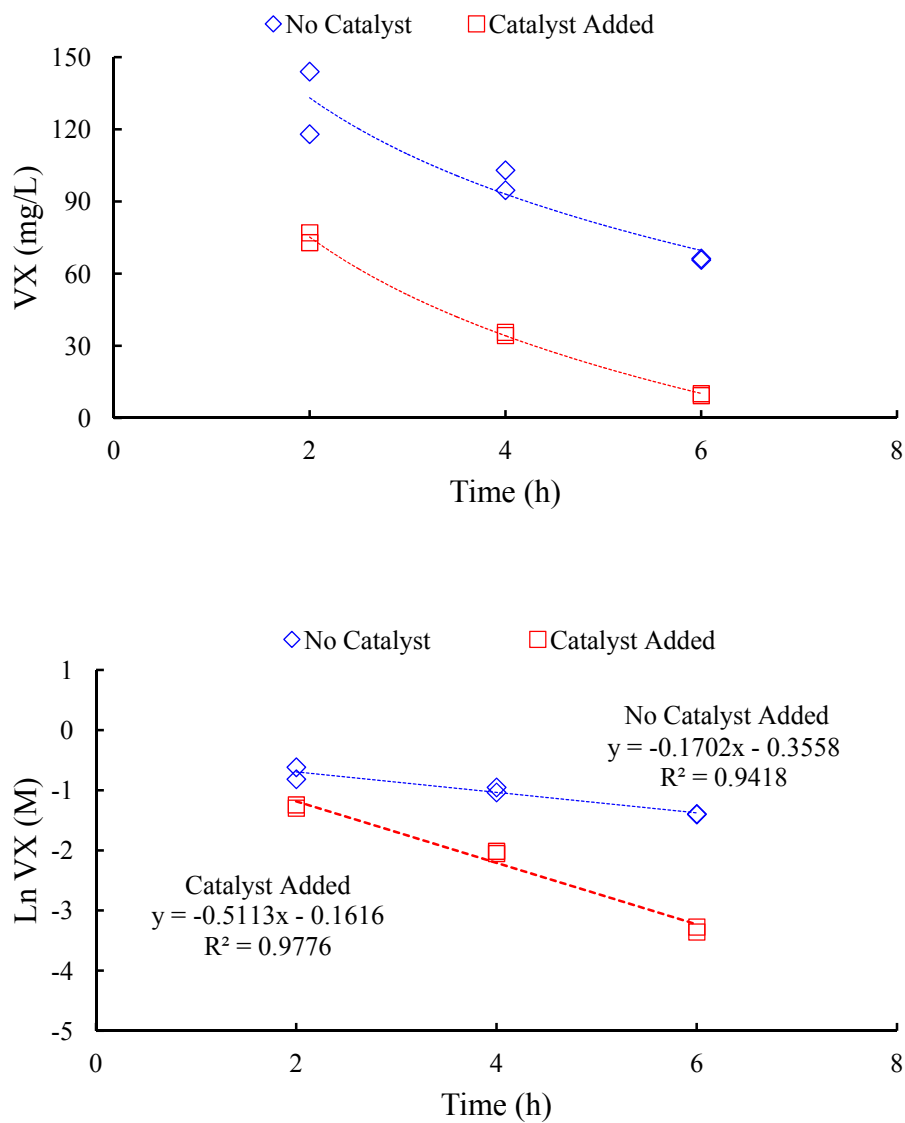


Figure 12. Residual VX as a function of time and catalyst. The VX loading was 10% and reactions were conducted at 30 °C Upper panel is the concentration profile and lower panel is the first-order plot.

4. CONCLUSIONS AND RECOMMENDATIONS

GB was successfully neutralized at 30 °C to less than the treatment goal of 1 mg/L when the GB loading was between 30 and 40% and the reaction time was 6 h. This is 3–4 times the typical loading of 10% used in EDS operations. During reactions conducted at 45 and 60 °C, GB was successfully neutralized to less than the treatment goal when the GB loading was between 40 and 50%. This is 3–5 times the typical GB loading of 10% used in EDS operations. In loadings over 40%, the neutralent became noticeably more viscous. At loadings $\geq 60\%$ and a reaction temperature of 60 °C, the neutralent became so viscous it could not be stirred. Additional studies should focus on measuring physicochemical parameters (such as viscosity) and product distribution at these higher GB loadings.

HD was successfully neutralized at 60 °C to less than the treatment goal of 50 mg/L when the HD loading was between 40 and 50% and the reaction time was 6 h. There were no apparent differences in efficacy when munitions or CASARM grade HD was used. This is 4–5 times the typical HD loading of 10% used in EDS operations. The treatment goal for HD was not met when the reactions were conducted at 30 and 45 °C using the lowest loading (20%) of HD. In loadings $> 50\%$, excessive heat and fumes were generated when the MEA was added to the HD. At loadings $\geq 80\%$, the neutralent became so viscous it could not be stirred. Additional studies should focus on measuring physicochemical parameters (such as enthalpy and viscosity) and product distribution at these higher HD loadings.

VX was not reduced below the treatment goal of 1 mg/L under any of the conditions evaluated during this study. In the 1 % VX loading experiments conducted at 60 °C for 6 h, the residual VX was approximately 3 times higher than the treatment goal of 1 mg/L. The viscosity of the final neutralents, while not determined, appeared to be positively correlated with agent loading. Additional studies should focus on the affect of higher reaction temperatures and measuring physicochemical parameters (such viscosity) and product distribution at these higher temperatures and VX loadings.

A commercially available lanthanum-based catalyst was found to be useful in accelerating the decomposition of VX, but not HD, when the reactions were conducted at ≤ 30 °C and a 10% agent loading. Using a first-order model, the solution half-life of VX was estimated to be 246 min without the catalyst and 84 min with the catalyst. Additional studies should focus on optimizing the reaction conditions (such as catalyst concentration and reaction temperature) to take advantage of the catalyst.

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LITERATURE CITED

1. Non-Stockpile Chemical Materiel Project; Fact sheet. U.S. Army Chemical Materials Agency, Public Outreach and Information Office: Edgewood, MD, 2005.
2. Chemical Weapons Destruction at the U.S. Army Pueblo Chemical Depot; Fact sheet. Pueblo Chemical Agent Destruction Pilot Plant, Public Outreach Office: Pueblo, CO, 2008.
3. Chemical Weapons Destruction at Blue Grass; Fact sheet. Blue Grass Chemical Agent Destruction Pilot Plant, Public Outreach Office: Richmond, KY, 2010.
4. Pueblo Chemical Depot, www.en.wikipedia.org/wiki/Pueblo_Chemical_Depot, accessed February 2012.
5. Blue Grass Army Depot, www.en.wikipedia.org/wiki/Blue_Grass_Army_Depot, accessed February 2012.
6. Explosive Destruction Technologies; Fact sheet. U.S. Army Element, Assembled Chemical Weapons Alternatives, Communications and Congressional Affairs Office: Edgewood, MD, 2010.
7. New Path Forward Charted for Explosive Destruction Technologies at Pueblo Chemical Depot; News release. Communications and Congressional Affairs Office, U.S. Army Element, Assembled Chemical Weapons Alternatives: Edgewood, MD, 13 September 2010; https://www.peoacwa.army.mil/wp-content/uploads/acwa_edt_press_release13sept10.pdf (accessed December 2013).
8. Explosive Destruction System Overview; Fact sheet. U.S. Army Chemical Materials Agency, Public Outreach and Information Office: Edgewood, MD, 2005.
9. Non-Stockpile Chemical Materiel Project – Celebrating a Treaty Milestone; Fact sheet. U. S. Army Chemical Materials Agency, Public Outreach and Information Office: Edgewood, MD, 2010.
10. Chemical Materials Activity Home page. www.cma.army.mil/pressroom, accessed February 2012.
11. Clarke, H.T. 4-Alkyl-1,4-Thiazans. *J. Chem. Society London* **1912**, 101, 1583–1590
12. Helfrich, O.B.; Reid, E.E. Reactions and Derivatives of β,β' -Dichloroethyl Sulfide. *J. Am. Chem. Soc.* **1920**, 42(6), 1208–1232.
13. Brankowitz, W.R. *Demilitarization of Mustard Agent (HD) at Fort McClellan, Alabama*; ARCSL-TR-7705; U.S. Army Armament Research and Development Command: Aberdeen Proving Ground, MD, 1978; UNCLASSIFIED Report (AD-A054740).

14. Yurow, H.W.; Davis, G.T. *Decontamination and Disposal Methods for Chemical Agents – A Literature Survey*; U.S. Army Armament Research and Development Command: Aberdeen Proving Ground, MD, 1982; UNCLASSIFIED Report (AD-B069586).
15. Petrov, V.G. *Technological Aspect of Realization of a New Concept of Chemical Disarmament in Russia*. Presented at the Chemical and Biological Medical Treatment Symposium – Industry II World Congress on Chemical and Biological Terrorism, Dubrovnik, Croatia, 20-28 April 2001. (AD-P0133411).
16. Durst, H.D. (Editor), *Evaluation of the Chemistry Which Supports VX Neutralization in the Munitions Management Device-1 (MMD-1)*, Comprehensive report prepared for the Project Manager for Non-Stockpile Chemical Materiel, Aberdeen Proving Ground-Edgewood Area, MD, October 1997.
17. Durst, H.D., Ed. *Evaluation of the Chemistry Which Supports HD Neutralization in the Munitions Management Device-1 (MMD-1)*. Project Manager for Non-Stockpile Chemical Materiel, U.S. Army Edgewood Research, Development, and Engineering Center: Aberdeen Proving Ground, MD, September 1997.
18. Durst, H.D., Ed. *Evaluation of the Chemistry Which Supports GB Neutralization in the Munitions Management Device-1 (MMD-1)*. Project Manager for Non-Stockpile Chemical Materiel, U.S. Army Edgewood Research, Development, and Engineering Center: Aberdeen Proving Ground, MD, October 1997.
19. Ayen, R.J. *Assessment of Explosive Destruction Technologies for Specific Munitions at the Blue Grass and Pueblo Chemical agent Destruction Pilot Plants*. National Academies Press: Washington, DC, 2009. ISBN: 978-0-309-12683-0.
20. *Explosive Destruction System Phase 1 Unit 2 Series Test Report for VX Testing*. U.S. Army Chemical Materials Agency, Project Manager for Non-Stockpile Chemical Materiel: Aberdeen Proving Ground, MD, Draft, November 2005.
21. *Test Chemistry and Analytical Method Precision and Accuracy Study Report for Nitrogen Mustard (HN-1 and HN-3)*. U.S. Army Chemical Materials Agency, Project Manager for Non-Stockpile Chemical Materiel: Aberdeen Proving Ground, MD, Final, April 2000.
22. Scheiman, M.A. *A Review of Monoethanolamine Chemistry*. NRL Report 5746; U.S. Naval Research Laboratory: Washington, D.C., 1962; UNCLASSIFIED Report (AD-277031).
23. *Methods for the Determination of Organic Compounds in Drinking Water: Supplement 1*; EPA-600/4-90/020; U.S. Environmental Protection Agency: Cincinnati, OH, July 1990. (EPA Method 506, pp 5–32).

24. Morrissey, K.M.; Connell, T.R.; Creasy, W.R.; Stuff, J.R.; Durst, H.D.; O'Connor, R.J. *Quantitative Analysis of VX in Caustic Neutralization Solutions by Solid Phase Extraction and GC/MSD: Analysis of Hydrolysates as Separated Organic and Aqueous Phases*; ECBC-TR-009; U.S. Army Soldier Biological Chemical Command: Aberdeen Proving Ground, MD, 1999; UNCLASSIFIED Report (AD-A360497).
25. Morrissey, K.M.; Connell, T.R.; Stuff, J.R.; Durst, H.D.; O'Connor, R.J. *Quantitative Analysis of VX in Caustic Neutralization Solutions by Solid Phase Extraction and GC/MSD: Analysis of Hydrolysate as Unseparated Phases*; ECBC-TR-010; U.S. Army Soldier Biological Chemical Command: Aberdeen Proving Ground, MD, 1999; UNCLASSIFIED Report (AD-A362643).
26. Waysbort, D.; McGarvey, D.J.; Creasy, W.R.; Morrissey, K.M.; Hendrickson, D.M.; and Durst, H.D. A Decontamination System for Chemical Weapons Agents using a Liquid Solution on a Solid Sorbent. *Journal of Hazardous Materials*, **2009**, 161(2-3), 1114–1121.
27. Morrissey, K.M.; Ruth, J.L.; Fouse, J.C.; Cheicante, R.L.; Flowers, A.K.; and Durst, H.D. *Cleaning of Residues from Equipment Surfaces After Demilitarization of Arsenical-Based Munitions and Fill Materials*; ECBC-TR-582; U.S. Army Soldier Biological Chemical Command, Aberdeen Proving Ground, MD, 2007. UNCLASSIFIED Report. (AD-A474404)
28. Morrissey, K.M.; Ruth, J.L.; Cheicante, R.L.; Schenning, A.M.; Fouse, J.C.; Hulet, M.S.; Creasy, W.R.; Durst, H.D.; O'Connor, R.J.; Berg, F.J.; McMahon, L.R.; Forrest, L.P.; Weiss, M.P. *Characterization and Neutralization of Recovered Lewisite Munitions*; ECBC-TR-531; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2006; UNCLASSIFIED Report (AD-A460761).
29. Morrissey, K.M.; Cheicante, R.L.; Connell, T.R.; Creasy, W.R.; Fouse, J.C.; Hulet, M.S.; Ruth, J.L.; Schenning, A.M.; Williams, B.W.; Durst, H.D.; O'Connor, R.J.; Winemiller, M.D.; McMahon, L.R.; McGuire, K.; Forrest, L.P.; Weiss, M.P.; Smith, P.B. *Characterization and Neutralization of Arsenical-Based WWII Era Chemical Munition Fills*; ECBC-TR-479; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2006; UNCLASSIFIED Report (AD-A455660).
30. Morrissey, K.M.; et al. *Search for a Universal Neutralization Reagent: Application to the Explosive Destruction System*; ECBC-TR-XXX; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2014. UNCLASSIFIED Report (In preparation).
31. Stuff, J.R.; Cheicante, R.L.; Morrissey, K.M.; Durst, H.D. Trace Determination of Isopropyl Methylphosphonofluoridate (GB) and Bis(2-Chloroethyl)Sulfide (HD) in Chemical Neutralization Solutions by Gas Chromatography-Mass Spectrometry. *J. Microcolumn Separations* **2000**, 12(2), 87–92.

32. Morrissey, K.M.; Williams, B.R.; Cheicante, R.L.; Stuff, J.R.; and Durst, H.D. *Quantitative and Qualitative Gas Chromatographic Analysis of Reaction Masses Produced from Chemical Neutralization of Isopropyl Methylphosphonofluoridate with Monoethanolamine*; ECBC-TR-041; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 1999. UNCLASSIFIED Report (AD-A368372).
33. Standard Operating Procedure, Neat Agent Purity Determination by Gas Chromatography Using Thermal Conductivity Detection, Analytical Chemistry Team Method 007, November 1997.
34. *Certificate of Analysis: HD*. Lot Number HD-U-3225-CTF-N. U.S. Army Research, Development and Engineering Command, Aberdeen Proving Ground, MD, February 2012.
35. Erney, D.R.; Gillespie, A.M.; Gilvydis, D.M.; Poole, C.F. Explanation of the Matrix Induced Chromatographic Response Enhancement of Organophosphorus Pesticides During Open Tubular Column Gas Chromatography with Splitless or Hot On-Column Injection and Flame Photometric Detection. *J. Chrom. A* **1993**, 638(1), 57–63.
36. Erney, D.R.; Pawlowski, T.M.; Poole, C.F. Matrix-Induced Peak Enhancement of Pesticides in Gas Chromatography: Is There a Solution? *J. High Res. Chrom.* **1997**, 20(7), 375–378.
37. Procell, L.R.; Sorrick, D.C.; Szafraniec, L.; Yang, Y-C.; Berg, F.J. *Neutralization of GB and VX in Monoethanolamine at Ambient Temperature*; ERDEC-TN-014; U.S. Army Edgewood Research Development and Engineering Center: Aberdeen Proving Ground, MD, 1996. UNCLASSIFIED Report (AD-E491759).
38. Procell, L.R.; Wagner, G.W.; Sorrick, D.C.; Butrow, A.B.; Abercrombie, P.L.; Yang, Y-C. *Effects of Process Variables on the HD-MEA Neutralization Process*. Presented at the 1998 ERDEC Scientific Conference on Chemical and Biological Defense Research: Aberdeen Proving Ground, MD, 17-20 November 1998.
39. Basab, B.D.; Edwards, D.R.; Neverov, A.A.; Brown, R.S. A Study of the Kinetics of La^{3+} Promoted Methanolysis of *S*-Aryl Methylphosphonothioates: Possible Methodology for Decontamination of EA 2192, the Toxic Byproduct of VX Hydrolysis. *Inorg. Chem.* **2011**, 50, 3071–3077.
40. Tamer, A.; Neverov, A.A.; Brown, R.S. Efficient Methanolytic Cleavage of Phosphate, Phosphonate and Phosphonothioate Esters Promoted by Solid Supported Lanthanide Ions. *Industrial and Engineering Chemistry Research* **2010**, 49, 7027–7033.
41. Neverov, A.A.; Brown, R.S. Development of Metal Ion Promoted Alcoholysis as a Rapid Methodology for the Destruction of Organophosphorus CW Agents, Their Simulants and Pesticides. *Main Group Chemistry* **2010**, 33, 265–281.

ACRONYMS AND ABBREVIATIONS

ACS	American Chemical Society
ASTM	ASTM International. Known as American Society for Testing and Materials until 2001
CAS	Chemical Abstracts Service
CASARM	Chemical Agent Standard Analytical Reference Material
CBARR	Chemical Biological Applications and Risk Reduction
CMA	U.S. Army Chemical Materials Activity
CTF	Chemical Transfer Facility
CWA	chemical warfare agent
CWM	chemical warfare materiel
DBAE	2-(dibutylamino) ethanol
DIW	ASTM Type I deionized water
DoD	U.S. Department of Defense
ΔS	entropy change
E_a	activation energy
ECBC	U.S. Army Edgewood Chemical Biological Center
EDS	Explosive Destruction System
ERDEC	U.S. Army Edgewood Research Development and Engineering Center
GB	sarin, isopropyl methylphosphonofluoridate
GC	gas chromatography
GC/TCD	gas chromatography/thermal conductivity detector
HD	sulfur mustard, bis(2-chloroethyl) sulfide
MEA	monoethanolamine
MSD	mass selective detector
NA	not applicable
NSCM	non-stockpile chemical materiel
PMNSCM	Product Manager for Non-Stockpile Chemical Materiel
QC	quality control
RCWM	recovered chemical warfare materiel
SSD	sample standard deviation
TCD	thermal conductivity detector
TSDF	treatment, storage, and disposal facility
VX	<i>O</i> -ethyl-S-[2- <i>N,N</i> -(diisopropylamino)ethyl]methylphosphonothioate

